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Performance prediction of the catalyst PR-81 at the production unit using mathematical modeling method

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Abstract

The performance analysis of the reforming catalyst PR-9 and its replacement prediction on the catalyst PR-81for production reforming unit L-35-11/450K have been carried out using a mathematical model. The effect of feedstock composition on product yield has been studied. It is shown that the feedstock composition decisively influences the yield and octane number. The model study have shown that the replacement for the PR-81 catalyst will increase the yield of 2.5-3.5% wt.

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Keywords: catalytic reforming; a mathematical model; Pt-Recatalyst; prediction; yield

1. Introduction

For more than 50 years the gasoline catalytic reforming has been used to produce high-octane gasoline and aromatic hydrocarbons, and is considered one of the basic processes of modern oil refinery. The determining factor is the whole process efficiency, stability, selectivity and activity of the Pt-catalysts used in reforming [1-6]. Methodical modeling bases for catalytic processes were laid by Russian scientists: G. K. Boreskov, member of the Academy of Sciences, and M. G. Slin'ko, RAS corresponding member, and foreign researchers: N. A. Amundson and R. Aris. The method is based on the approach of complex chemical and technological process decomposition

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into a number of components (physical and chemical), their divided study, followed by a synthesis of the general mathematical model from the mathematical models of separate parts of a complex process [7-11].

The aim of this study is to predict the PR-81 catalyst charge effectiveness on the production reforming unit L-35-11/450K.

2. Study subject

Catalytic reforming unit L-35-11/450K with a preliminary hydrotreating is an important subject of "Komsomolsk Refinery" JSC in the Far East of Russia. Previous foreign catalyst charge PR-9 («Criterion» company) has proven to be appropriate in operation and ensure high specified quality yield. Results of the new catalyst PR-81 (IHP SB RAS) were modeled on the mathematical model, and the results of the catalyst replacement effect on the main industrial process indicators were predicted. The results of chromatographic analysis of the hydrocarbon feedstock composition, technological modes of production unit operation were used as source data. Table 1 shows the main indicators of reforming production unit charged with catalyst PR-81 and PR-9.

Table 1. Main indicators of reforming units L-35-11/600 and A-35-11/ 450K on catalysts PR-81 and PR-9, respectively.

Indicators/catalysts	PR-81	PR-9
Pressure, Mpaa	2.6-2.7	1.6-1.7
Reactors inlet temperature, °C	498-502	470-490
Reactor temperature drop, °C	72/30/5	67/33/15/9
Hydrogen concentration in HBG, % vol.	77-79	84-86
Stable reformate yield % wt. (calculation)	87-88	84-86
Hydrogen yield, % wt.	2.1-2.2	1.8-1.9
Reformate octane number, RON	94-95	94-95

3. Methods

The studies have been carried out using a mathematical model, which allows to analyze changes in the product obtained by the catalyst replacement [12-15]. The nonstationary kinetic model of catalytic reforming process enables to consider physical and chemical laws of hydrocarbons conversion on the catalyst surface [12, 13], and changes in the composition feedstock. As is known, the catalyst does not displace the equilibrium position, its role is to increase the reaction rate. This permits to conduct comparative evaluation of the activity, selectivity and stability of different catalysts on the rate constants of the target and side reactions.

The method of mathematical modeling allows to determine the rate constants of chemical reactions on different catalysts by solving the inverse kinetic task on the basis of experimental data (concentration of separate hydrocarbons in the feedstock and catalysate) using the developed reforming model [3]

$$\frac{k_1}{k_2} = e^{\frac{E_1 - E_2}{RT}}, \quad (1)$$

where k_1, k_2 are reaction rate constants on catalysts 1 and 2; E_1, E_2 are activation energy on the catalysts 1 and 2. In the paper, the inverse kinetic task was solved by numerical method of the reaction rate constants for the minimum difference calculation between the calculated concentration value on the model and the experimental data.

The studies were conducted in two stages:

- determination of chemical reactions rate constants for the new catalyst;
- modeling the catalyst replacement on reforming unit with a fixed bed of the catalyst on a mathematical model.

4. Results and discussion

Using the mathematical model described above results of previously catalyst charge PR-9 were analyzed, and results for PR-81 catalyst replacement for the main catalytic reforming process indicators were predicted. The results are presented in Fig. 2 and Table. 2-6.

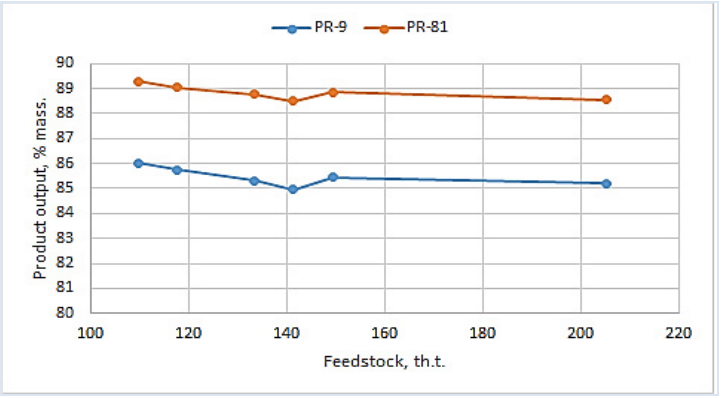

Fig.1. The product yield in relation to the feedstock and various catalysts.

Feedstock composition effect on the yield was studied (Table 2). As can be seen from Table 2, the hydrocarbon feedstock composition determines the yield and octane number. From the table it can be traced that by using the same technological indicators, but different hydrocarbon feedstock composition a different level of yield and octane number is achieved. For example, there is in the highest reformate yield using the feedstock 1 in comparison to the rest feedstocks (89.59 wt.%). Component feedsrock content used in the L-35-11/450K is shown in Table 3.

Table 2. The effect study of feedstock composition PR-81 catalyst charge for the same amount of processed feedstock 205.301 tonnes (model calculation).

Feedstock	Feedstock 1	Feedstock 2	Feedstock 3	Feedstock 4	Feedstock 5	Feedstock 6
Hydrogen, %	87.8	87.8	87.8	87.8	87.8	87.8
Hydrogen yield, %	1.91	1.94	1.96	1.98	1.8900	1.96
Steam/(Naphtha +Aromatics)	0.82	0.77	0.90	0.95	0.90	0.94
n-Steam/i-Steam feedstock	0.66	0.75	0.70	0.72	0.67	0.66
Crude naphtha ,%wt.	1.9	1.85	1.83	1.80	1.94	1.85
Octane number	94.8	94.9	94.6	94.6	94.5	95
Reformate yield, %wt.	89.59	89.2	88.9	88.7	89.09	88.56

Table 3. The hydrocarbon feedstock composition (model calculation).

Component	Feedstock 1	Feedstock 2	Feedstock 3	Feedstock 4	Feedstock 5	Feedstock 6
nC6	2.95	2.77	2.86	2.69	3.2	1.84
nC7	3.81	3.54	3.77	4.06	3.65	3.91
nC8	5.48	5.89	5.97	6.41	5.69	6.02
nC9	3.27	3.58	3.86	4.3	3.6	4.24

nC10	2.23	2.4	2.5	2.57	2.6	2.81
∑	17.74	18.18	18.96	20.03	18.74	18.82
iC5	0	0	0	0	0	0.13
iC6	2.28	1.63	1.7	1.42	2.19	1.06
iC7	2.11	1.48	1.94	2.14	1.88	2.5
iC8	8.31	6.07	8.18	7.96	8.09	8.02
iC9	6.19	6.75	6.68	7.16	6.57	7.02
iC10	7.81	8.39	8.74	8.98	9.09	9.84
∑	26.7	24.32	27.24	27.66	27.82	28.57
ZP	0.07	0.04	0.04	0.03	0.06	0.05
MZP	2.53	2.69	2.67	2.57	2.81	2.01
DMZP	3.4	2.78	3.09	3.27	3.05	3.34
ZG	0.69	0.89	1.06	0.98	0.88	1.12
MZG	6.8	6.53	6.36	6.3	6.15	5.98
C8H	12.24	14.93	12.52	12.22	11.69	11.97
C9H	7.57	7.64	7.11	7.39	7.32	7.75
C10H	1.12	1.2	1.25	1.28	1.3	1.41
∑	34.42	36.7	34.1	34.04	33.26	33.63
BENZ	0.54	0.48	0.43	0.36	0.48	0.27
TOLY	3.87	3.4	3.14	2.56	3.1	2.4
KSIL	7.98	7.53	6.66	6.41	6.98	6.34
AP9	5.46	5.31	5.39	5.25	5.95	5.98
AP10	1.82	1.77	1.8	1.75	1.99	1.99
∑	19.67	18.49	17.42	16.33	18.5	16.98

PR-81 catalyst performance results the product yield with different octane numbers (96 and 98) are obtained in the model. The results are presented in Tables 4-5. The studies show that the catalyst will remain active in the range of 0,80-0,84 relative units. To obtain the product with RON 98 a high inlet temperature (up to 498) must be maintained which is connected with an increase in the crude naphtha accumulation on the catalyst (1.5 wt.% more than in the product yield with RON 96).

Table 4. PR-81 catalyst performance prediction in the product yield with RON = 96.

Processed feedstock, th. tonnes.	313.608	316.368	382.638	417.738	454.008	489.108	525.378
Hydrogene yield, %	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Output temperature	480	481	481	481	481	483	483
Feedstock consumption, m3/h	65	65	65	65	65	65	65
Crude naphtha, %wt.	2.66	2.86	3.1	3.36	3.63	3.93	4.25
Octane number	96	96.1	96.1	96	95.9	96.1	96.1

Table 5. PR-81 catalyst performance prediction in the product yield with RON = 98.

Processed feedstock, th. tonnes	313.608	346.368	382.638	417.738	454.008	489.108	525.378

Hydrogene yield, %	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Output temperature	486	487	488	488	488	488	488
Crude naphtha, %wt.	3.07	3.41	3.81	4.26	4.76	5.26	5.79
Octane number	98	98	97.9	98.1	98.1	98	97.9

Table 6 shows the constants relative values of the chemical reactions (one unit means the foreign catalyst values). The Table demonstrates that the PR-81 contact allows faster dehydrocyclization of normal and iso-paraffins into the six-membered naphthenes. Paraffins hydrocracking reactions have a slower rate. Taking this into account, we can conclude that PR-81 catalyst possesses higher dehydrocyclization properties, which helps to increase the specified quality product yield under similar technological conditions as ion platinum increases the rate of cyclopentanes isomerization and alkanes dehydrocyclization.

Table 6. The relative rate constants of chemical reactions, relative units.

Chemical reaction	Constant value
hydrocracking n-P	0.5
isomerization n-P into iso-P	1.5
dehydrocyclization n-P into N-6	1.3
hydrocracking iso-P	0.8
dehydrocyclizatio iso-P into N-6	1.1
hydrogenating N-5 into iso-P	1.0
isomerization N-5 into N-6	2.0
dehydrogenating N-6 into Ar	1.0

5. Conclusion

Application of the mathematical modeling method for catalyst replacement predicting at the production unit with a fixed bed catalyst has showed that:

- • PR-81 catalyst has high performance and can ensure high specified quality product yield;
- • catalyst replacement will increase the yield of 2.5-3.5% wt.;
- • a higher dehydrocyclization reaction rate provides yield up to 89.5% wt. with RON = 95, which is a good advantage of the platinum contact.

References

[1]J.H. Jenkins, T.W. Stephens. Hydrocarbon Process. (November); 1980; p. 163–167.
[2] U. Taskar, J.B. Riggs. Modeling and optimization of a semiregenerative catalytic naphtha reformer. AIChE J. 3 (№43); 1997; p. 740–753.
[3] H.G. Krane, A.B. Groh, B.L. Shulman, J.H. Sinfelt. Reactions in Catalytic Reforming of Naphthas. World Petroleum Congress; 1960; p. 39–53.
[4] J. Henningsen, M. Bundgaard-Nielson. Catalytic reforming. Br. Chem. Eng. 15 (11); 1970; p. 1433–1436.
[5] G.J. Antos, A.M. Aitani. Catalytic Naphtha Reforming. Marcel Dekker; 2004; p.602.
[6] A. Aitani. Catalytic naphtha reforming. Encyclopedia of Chemical Processing; 2006; p. 397–406.
[7]G.B. Marin, G.F. Froment.Reforming of C6 hydrocarbons on a Pt-Al2O3 catalyst. Chem. Eng. Sci. 37 (5); 1982; p. 759–773.
[8] R.B. Smith, Kinetic analysis of naphtha reforming with platinum catalyst, Chem.Eng. Prog. 55 (6) (1959) 76–80.
[9] A.S. Noskov. Two centuries of mathematical modelling. Report at the problem seminar on 90-th anniversary of M.G. Slinko; 2005.
[10] D. Bommannan, R.D. Strivastava, D.N. Saraf. Modeling of catalytic naphtha reformers. Can. J. Chem. Eng. 67; 1989; p. 405–411.
[11] M.S. Gyngazova, A.V. Kravtsov, E.D. Ivanchina, M.V. Korolenko, D.D. Uvarkina, Kinetic model of the catalytic reforming of gasolines in moving-bed reactors Catalysis in industry, vol. 2, No. 4(2010) 374-380.

[12]Inna V. Yakupova, Ekaterina S. Sharova, Emilia D. IvanchinaMathematical modelling method application for optimization of catalytic reforming process, Procedia Chemistry, Vol.10 (2014) 197-202.
[13] Inna V. Yakupova, Ekaterina S. Sharova, Emilia D. Ivanchina Computer modelling system application for catalytic reforming unit work optimization,
Procedia Chemistry, Vol.10 (2014) 192-196.
[14] Je.D. Ivanchina, M.S. Gyngazova, A.S. Belyj, M.D. Smolikov, V.I. Prodan, M.S. Shirokova. Analiz jeffektivnosti zameny katalizatora na ustanovke kataliticheskogo riforminga L-35/11 – 1000, Neftepererabotka i neftehimija, №10 (2013) 18 – 23.
[15] Je.D. Ivanchina, E.S. Sharova, A.G. Koksharov, S.A. Faleev, A.I. Fedjushin Optimizacija rezhimov raboty katalizatorov riforminga s ispol'zovaniem metoda matematicheskogo modelirovanija, Neftepererabotka i neftehimija, №10(2014)25 – 29